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The calculation of potential curve of $A^1\Sigma^+$ state of ^{7}LiH from experimental data

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Abstract . New Rydberg-Klein-Rees (RKR) potential energy curve calculations of the $A^1\Sigma^+$ state of ^{7}LiH have been made from v = 0 to 26

Keywords $A^1\Sigma^+$ state of LiH, RKR potential, calculation from experimental data

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The Rydberg-Klein-Rees [1,2,3] or RKR method is a widely used method for determining the potential curves of diatomic molecules from experimental vibrational and rotational spectroscopic term values. This work describes the RKR potential curve calculations of the $A\ ^1\Sigma^+$ state of ^{7}LiH. This state has been of interest to spectroscopists due to its anomalous character where its vibrational energy intervals increases with increasing v to a maximum and then begin to fall monotonically. The analogous states of KH and NaH show similar behavior and their RKR calculations have recently been reported [4,5]. The RKR calculations of the $A\ ^1\Sigma^+$ state of ^{7}LiH from $v = 0$ to 26 in two separate attempts but, somehow, did not make the potential curve calculations in this region. To our knowledge, these calculations have not so far appeared in literature. We have therefore undertaken to perform these RKR calculations of the $A\ ^1\Sigma^+$ state of ^{7}LiH from $v = 0$ to 26 based on the data of Rafi *et al* [8].

The RKR method determines the classical turning points R_{max} and R_{min} for a vibrational level. It is well known that

$$R_{max}(v) = \left(\frac{f(v)}{g(v)} + f(v)^{1/2} \right)^{1/2} + f(v),$$
$$R_{min}(v) = \left(\frac{f(v)}{g(v)} + f(v)^2 \right)^{1/2} - f(v), \qquad (1)$$

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where

$$f(v) = \left(\frac{\hbar}{4\pi c\mu}\right)^{-1/2} \int_{-1/2}^{v} [G(v) - G(x)]^{-1/2} dx$$

$$= \frac{1}{2}\left(R_{max}(v) - R_{min}(v)\right), \tag{2}$$

$$g(v) = \left(\frac{4\pi c\mu}{\hbar}\right)^{1/2} \int_{-1/2}^{v} B(x)[G(v) - G(x)]^{-1/2} dx$$

$$= \frac{1}{2}\left(\frac{1}{R_{min}(v)} - \frac{1}{R_{max}(v)}\right).$$

$B(x)$ and $G(x)$ are the rotational constants and vibrational energy for level x. The potential energy curve can thus be constructed by substituting constants available from the analysis of experimental data in eqs.(1) and (2). Spectroscopic constants used in constructing the RKR curve of an electronic state are found from the Dunham-like expressions. These expressions for $B(v)$ and $G(v)$ are given by

$$B(v) = \sum_{i\geq 0}^{n} Y_{i1}(v+1/2)^i \tag{3}$$

$$= Y_{01} + Y_{11}(v+1/2) + Y_{21}(v+1/2)^2 + Y_{31}(v+1/2)^3 + \ldots\ldots,$$

$$G(v) = \sum_{i\geq 1}^{n} Y_{i0}(v+1/2)^i \tag{4}$$

$$= Y_{10}(v+1/2) + Y_{20}(v+1/2)^2 + Y_{30}(v+1/2)^3 + \ldots\ldots .$$

Dunham [9] also gave an expression of a non-vanishing term Y_{00} which in terms of the other constants is

$$Y_{00} = \frac{Y_{01}}{4} - \frac{Y_{10}Y_{11}}{12Y_{01}} + \frac{(Y_{10}Y_{11})^2}{144(Y_{10})^3} + \frac{Y_{20}}{4} . \tag{5}$$

Zero point energy (ZPE) for an anharmonic oscillator is thus given as

$$ZPE = G(0) + Y_{00}, \tag{6}$$

where

$$G(0) = \frac{Y_{10}}{2} + \frac{Y_{20}}{4} + \frac{Y_{30}}{8} + \frac{Y_{40}}{16} + \ldots\ldots. \tag{7}$$

The observed $B(v)$ values are fitted to a polynomial in $(v + 1/2)$ in eq (3) by least square fit program and the constants Y_{01}, Y_{11}, Y_{21}, Y_{31}, ... are obtained. Similarly, the constants Y_{10}, Y_{20}, Y_{30}, ... are obtained from the observed $G(v)$ values from eq. (4).

The RKR method consists of accurate evaluation of the integrals appearing in eq. (2) for which the integrand is singular at the upper limit of the integration. A number of numerical techniques for evaluating Klein integrals have been proposed in the 1960's and in particular computer program devised by Zare [10] became quite common. But the limitation of this method was that it gave crude treatment of the (integrable) singularities in the integrands of the Klein integrals. In 1972 new methods [11-13] of evaluating the Klein integrals appeared and the method of Tellinghuisen [14] proved simple and of high potential accuracy. In 1992, Le Roy [15] gave a computer program based on the quadrature procedure suggested by Tellinghuisen and included a number of improvements not included in the previous codes. The improved ability to give accurate results for energies near dissociation and an automatic procedure for smoothing the upper part of the inner wall of directly calculated RKR potentials are improtant features of the Le Roy program and has an advantage over other previous programs in making accurate

Table 1. RKR potential energy curve of the $A^1\Sigma^+$ state of $^7LiH^*$

v	$G(v) + Y_{(0)}$ (cm^{-1})		R_{min} (Å)		R_{max} (Å)	
	a	*b*	*a*	*b*	*a*	*b*
v_{min}**	0 00	0 00	2.5945	2 5963	2.5945	2 5936
-1/2***	7 260	7 406	–	–	–	–
0	131 81	131 26	2.2231	2.2252	3.0183	3.0087
1	412.71	412 28	2.0239	2 0242	3 2959	3 2831
2	725.48	725 25	1 9079	1.9080	3 4789	3 4685
3	1061.31	1060.94	1.8235	1 8244	3 6268	3.6192
4	1414 22	1413 74	1.7570	1 7589	3.7568	3 7514
5	1780 01	1779 57	1 7023	1 7050	3.8766	3.8724
6	2155 47	2155 19	1 6562	1 6589	3 9900	3.9864
7	2538.04	2537.91	1 6167	1 6189	4.0994	4.0960
8	2925 49	2925 47	1 5821	1 5839	4.2062	4.2029
9	3315.87	3315.89	1.5513	1 5528	4.3116	4 3082
10	3707 37	3707.44	1 5235	1.5249	4.4165	4 4130
11	4098 36	4098 53	1.4981	1 4994	4.5214	4 5180
12	4487.31	4487 70	1 4745	1.4758	4 6271	4.6239
13	4872.85	4873 61	1 4525	1.4541	4.7342	4 7314
14	5253.67	5254.97	1 4319	1 4342	4.8433	4 8410
15	5628 53	5630 47	1 4126	1 4162	4 9552	4.9538
16	5996.20		1 3947		5.0709	
17	6355.41		1.3782		5.1915	
18	6704.70		1.3631		5 3185	
19	7042.39		1 3492		5 4539	
20	7366.37		1.3362		5.6005	
21	7673 99		1.3241		5.7628	
22	7961.95		1.3132		5.9475	
23	8226.14		1.3032		6 1648	
24	8461 71		1.2946		6.4309	
25	8663.19		1.2873		6 7728	
26	8824.95		1.2815		7.2402	

a This work

b Values of Vidal and Stwalley [6]

* Spectroscopic contants of Rafi *et al* [8] are used

$v = v_{min}$ corresponds to potential curve minima.

** $v = -½$ corresponds to the energy $G(v) + Y_{(0)}$ where $G(v) = 0$ for $v = -½$.

RKR calculations right to the dissociation limit. We used the computer program of Le Roy [14] to make the RKR calculations of the A $^1\Sigma^+$ state of ^{7}LiH from $v = 0$ to 26. The Dunham-like coefficients used in these calculations are taken from Rafi *et al* [8]. Table 1 shows the values of R_{max} and R_{min} thus obtained from $v = 0$ to 26 along with the values of Vidal and Stwalley [6] from $v = 0$ to 15. The comparison of the two values from $v = 0$ to 15 gives the average difference of R_{max} and R_{min} to be 0.0017 ± 0.0009Å and 0.005 ± 0.0033 Å respectively. Figure 1 shows the two RKR curves – one of this work and the other of Vidal and Stawlley [6]. To conclude, the RKR potential energy curve of the A $^1\Sigma^+$ state of ^{7}LiH has been calculated from $v = 0$ to 26, for the first time, to our knowledge.

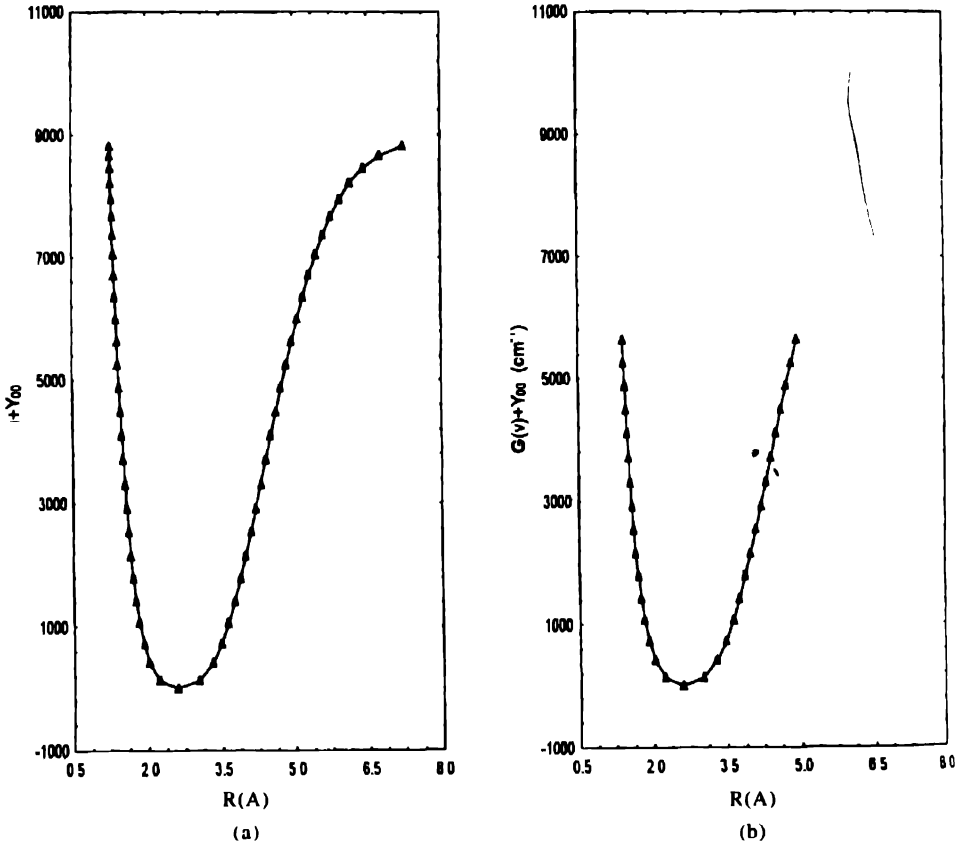

Figure 1. The RKR potential energy curves of the A $^1\Sigma^+$-state of ^{7}LiH : (*a*) This work, (*b*) Vidal and Stwalley [6]

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